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(54) Title: BREATHABLE NON-WETTABLE MELT-BLOWN NON-WOVEN MATERIALS AND PRODUCTS EMPLOYING THE SAME

(57) Abstract: Breathable non-wettable non-woven materials include a mass of melt-blown, non-woven fibers formed of a terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride monomers. Most preferably, the materials of the present invention are in the form of fabric structures which can be processed to form a variety of products for numerous end use applications, such as for garments, bandages, barrier vents, filter media and the like. In especially preferred form, the melt-blown non-woven fibers are comprised of a THV terpolymer formed of between about 30 to about 70 wt.% of tetrafluoroethylene monomer, between about 10 to about 20 wt.% of hexafluoropropylene monomer, and between about 20 to about 65 wt.% vinylidene fluoride monomer.

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**BREATHABLE NON-WETTABLE MELT-BLOWN NON-WOVEN
MATERIALS AND PRODUCTS EMPLOYING THE SAME**

FIELD OF THE INVENTION

5 The present invention relates generally to non-woven materials (e.g., fabric structures). In particularly preferred embodiments, the present invention relates to breathable non-woven melt-blown materials having oleophobic and/or hydrophobic properties.

BACKGROUND AND SUMMARY OF THE INVENTION

10 There are numerous fields of use whereby breathable fabric structures having oleophobic and/or hydrophobic properties are desired. For example, such fabric structures are highly desirable to form surgical drapes and gowns, wound dressings/bandages, outer garments, and barrier vents.

15 Currently, there are several products on the market that provide breathable protective garments for use during surgery. This breathability is typically expressed as a material's moisture vapor transmission rate (MVTR). Typical MVTR ranges for such protective garments are between about 1,000 to about 10,000 grams of water per square meter per 24 hours ($\text{g/m}^2/24\text{hrs}$). However, a person's body heat tends to increase
20 beneath the garments to a point whereby they become uncomfortable to wear. A surgical drape or gown having the ability to repel low surface tension fluids (for example, fluids having a surface tension of less than about 42 dynes/cm) and having an MVTR in excess of 100,000 $\text{g/m}^2/24\text{hrs}$ would be quite desirable to those wearing the garments but
25 which to date has not been made available.

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It is also known that one common problem with conventional wound dressings is that, to provide for an adequate barrier against airborne pathogens, barrier films with little or no MVTR are employed. This minimal MVTR creates a situation where sufficient amounts of moisture produced by the human body underneath a bandage cannot be removed and, as a result, maceration of the skin surrounding the wound occurs. This maceration can lead to prolonged healing times. It would therefore be quite desirable for a bandage material to have a MVTR in excess of about 100,000 g/m²24 hrs so as to prevent such maceration from occurring as well as to provide the wearer with a more comfortable bandage. To date, however, bandage materials which satisfy these requirements have not been offered.

Conventional water-proof and breathable outerwear garments provide significant improvements in wearer comfort over non-permeable materials that may be used (e.g., polyvinylchloride (PVC) films). However, any moderate to strenuous activity causes a rapid increase in temperature beneath these garments thereby causing great discomfort. A garment that was made from fabric materials that are non-wettable by fluids having surface tensions of less than about 42 dynes/cm and having MVTR's of greater than 100,000 g/m²/24hrs would be a significant improvement in wearer comfort. Again, however, such garment fabrics have not been provided to date.

Finally, there are many applications where fluids of various surface tensions need to be contained or prevented from entering designated areas while at the same time permit airflow to occur. Traditional barriers are made from polymeric materials that have either hydrophobic and/or oleophobic properties. Often, these properties are rendered onto a polymeric material by a secondary process which can add cost and

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typically results in non-uniform coatings that result in an unacceptable rate of failures. A barrier vent with inherent surface energies of less than about 30 dynes/cm and having the ability to allow for bulk airflow (e.g., Gurley densiometer readings of less than 600 seconds for a one square inch orifice, 100 cc of air and 5 ounce cylinder) would be quite desirable, but to date has not been provided. Expressed in other units an air permeability in excess of $0.045 \text{ ft}^3/\text{ft}^2/\text{min}$ at a differential pressure of 2163 Pascals would be desirable.

As can be appreciated from the preceding discussion, what has been needed are fabric structures which exhibit oleophobicity and/or hydrophobicity characteristics while, at the same time, are capable of allowing bulk air flow. It is towards fulfilling such needs that the present invention is directed.

Broadly, the present invention is embodied in materials comprised of a mass of melt-blown non-woven fibers comprised of a terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride monomers. Most preferably, such materials are in the form of fabric structures which can be processed to form a variety of products for numerous end-use applications, such as for garments, bandages, barrier vents, filter media and the like. In especially preferred form, the melt-blown non-woven fibers are comprised of a THV terpolymer formed of between about 30 to about 70 wt.% of tetrafluoroethylene monomer, between about 10 to about 20 wt.% of hexafluoroethylene monomer, and between about 20 to about 65 wt.% vinylidene fluoride monomer.

These and other aspects and advantages will become more apparent after careful consideration is given to the following detailed description of the preferred exemplary embodiments thereof.

DETAILED DESCRIPTION OF THE INVENTION

I. Definitions

As used herein and in the accompanying claims, the following terms are intended to have the definitions which follow:

5 "Breathable" or "breathability" mean that a fabric structure is capable of exhibiting a moisture vapor transmission rate (MVTR) of greater than about 100,000 g/m²/24hrs.

"Non-Wettable" or "non-wettability" means that a fabric structure is not wetted by a fluid having a surface tension of less than about 42
10 dyne/cm. Thus, for example, "non-wettable" fabric structures in accordance with the present invention will have an oil rating according to AATCC Test Method 118-1997 of at least 1.

"Bulk airflow" means that a fabric structure exhibits a porosity of less than about 600 Gurley-seconds, when employing a Gurley
15 densiometer having a one square inch orifice, 100 cc of air and 5 ounce cylinder. Alternatively, the term "bulk airflow" means that a fabric structure exhibits an air permeability in excess of 0.045 ft³/ft²/min at a differential pressure of 2163 Pascals.

II. Detailed Description of Preferred Exemplary Embodiments

20 The non-woven materials (e.g., fabric structures) of the preferred embodiments according to the present invention may be prepared from a terpolymer of tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride (hereinafter referred to as "THV polymer"). Preferably, the terpolymer includes from about 20 or less to about 65 wt. % or more
25 vinylidene fluoride, more preferably from about 25, 30, or 35 to about 40,

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45, 50, 55, or 60 wt. % vinylidene fluoride, and most preferably about 36.5 wt. % vinylidene fluoride. Preferably, the terpolymer includes from about 30 or less to about 70 wt. % or more tetrafluoroethylene, more preferably from about 35 or 40 to about 45, 50, 55, 60, or 65 wt. %

5 tetrafluoroethylene, and most preferably about 44.6 wt. %

tetrafluoroethylene. Preferably, the terpolymer includes from about 10 or less to about 20 wt. % or more hexafluoropropylene, more preferably from about 11, 12, 13, 14, 15, 16, 17, or 18 to about 19 wt. %

hexafluoropropylene, and most preferably about 18.9 wt. %

10 hexafluoropropylene.

Suitable THV polymers that may be employed in the practice of the present invention include Dyneon™ Fluorothermoplastics available from Dyneon LLC of Oakdale MN. Particularly preferred is Dyneon THV Grade E-15125 "O". This grade has a melting point of 164 C, a melt flow rate of

15 >200 (265 C/5Kg), a specific gravity of 2.004 g/cm³, a tensile at break of 9.9 Mpa, and an elongation at break of 273 %. Other Dyneon™

fluorothermoplastic terpolymers include Dyneon™ THV 220, Dyneon™ THV 410, Dyneon™ THV 500, and Dyneon™ THV X 610. The Dyneon™ fluorothermoplastic terpolymers with higher melt flow rates are preferred

20 due to the ease with which satisfactory melt blown webs may be prepared. The Dyneon™ fluorothermoplastic terpolymers with higher numbers, e.g., THV 410, THV 500, and THV X 610, have progressively higher percentages of tetrafluoroethylene. The higher the percentage of tetrafluoroethylene, the tougher it is to melt the polymer hence making it

25 more difficult to melt blow.

The melt-blown fibers may include a single THV polymer or combinations or blends of a THV polymer and one or more additional

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polymers. Alternatively (or additionally) discrete fibers formed of such other polymers may be melt-blown concurrently with or subsequently to the THV polymer so as to form a non-woven fibrous blend of THV and such other polymers or fibrous layers formed predominantly of the THV and such other polymers, respectively.

The additional polymers that may be employed in the practice of the present invention include another fluorothermoplastic terpolymer, or any other suitable polymer. Suitable polymers may include any suitable homopolymer, copolymer, or terpolymer, including but not limited to polysulfone, polyethersulfone (PES), polyarylsulfone, fluorinated polymers such as polyvinylidene fluoride (PVDF), polyolefins including polyethylene and polypropylene, polytetrafluoroethylene (PTFE or Teflon™), poly(tetrafluoroethylene-co-ethylene) (ECTFE or Halar™), acrylic copolymers, polyamides or nylons, polyesters, polyurethanes, polycarbonates, polystyrenes, polyethylene-polyvinyl chloride, polyacrylonitrile, cellulose, and mixtures or combinations thereof.

The fluorothermoplastic terpolymer may be subjected to a pretreatment, for example grafting or crosslinking, prior to melt blowing, or may be subjected to a post-treatment, for example grafting or crosslinking, after a melt blown web is made. There is no particular molecular weight range limitation for the THV polymer. Likewise, there is no particular limitation on the weight ratio of the tetrafluoroethylene, hexafluoropropylene, and vinylidene fluoride monomers in the THV polymer. Various molecular weights and/or different monomer ratios may be preferred for melt blown webs to be used for certain applications.

The materials of the present invention are melt-blown non-woven structures. In this regard, the preferred THV polymers may be melt-blown

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using virtually any conventional melt-blowing technique to make sheets, tubes, cylinders and like structural forms for a variety of end use applications. Thus, for example, the materials of the present invention are most preferably a mass of melt-blown non-woven fibers, which fibers as noted above are most preferably formed of a THV polymer. Non-woven materials of the present invention may be made using conventional melt-blowing techniques described more fully in U.S. Patents Nos. 3,776,796; 3,825,379; 3,904,798; 4,021,281; and 5,591,335 (the entire content of each such cited patent being incorporated expressly hereinto by reference).

The diameters of the melt-blown THV fibers forming the non-woven materials of the present invention are not critical. Thus, average fiber diameters of less than 500 μm , and preferably less than 100 μm , and typically less than 50 μm may be melt-blown if desired. Most preferably, the fibers have an average diameter which is greater than about 1 μm , and more preferably greater than about 5 μm .

Following production, the non-woven fabrics may be fashioned into a variety of products, for example, garments (e.g., surgical or other similar medical gowns, drapes and the like), bandages, and bulk airflow barrier vents. Thus, the fabrics of this invention may be mated (e.g., by sewing, gluing and the like) to one or more other woven, non-woven or knit fabric structures to suit virtually any end use application where the non-wettable and breathable properties of the fabric structures of this invention are needed.

The present invention will be further understood from a review of the following non-limiting Examples.

III. Examples

A THV polymer (Grade E-15125 "O") obtained commercially from Dyneon, LLC and having the following properties was employed in the Examples:

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THV Polymer Properties:

Form: Pellets
 Melting range: 164°C - ASTM D4591)
 Melt Flow Index: >200 (265°C/5 kg) – ASTM D1238
 Specific Gravity: 2.004 g/cc – ASTM D792
 Tensile @ break: 9.9 Mpa (1,435 psi) – ASTM D638
 (film)
 Elongation @ break: 273% - ASTM D638

Seven melt-blown fabric samples, identified below by Sample Nos. 1.1 through 1.7, were made using the process conditions in Table 1A using a melt-blowing die having a width of 152 mm and a die temperature of 249°C.

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Table 1A

Sample No.	Polymer Throughput, kg/hr	Line Speed, m/min	Die to Coll. Distance, m	Air Pressure, Kpa (1.52 mm air gap, 60°)	Air Temp, °C	Die Pressure, Kpa
1.1	3.46	6.1	0.254	41.4	248	1159
1.2	3.90	6.1	0.356	13.8	256	1063
1.3	3.90	6.1	0.356	13.8	247	1132
1.4	3.90	3.96	0.356	13.8	248	1159
1.5	3.90	3.96	0.203	13.8	247	1311
1.6	5.40	3.35	0.203	13.8	239	2677
1.7	5.40	3.35	0.203	27.6	243	2415

Samples 1.1, 1.5, 1.6 and 1.7 were subjected to physical property measurements. The results appear in Table 1B below.

Table 1B

Sample No.	Air Permeability, $\text{m}^3/\text{m}^2/\text{min}$	Basis Wt., g/m^2	Thickness, mm	Avg. Fiber Diameter, μm
1.1	60.43	76.9	0.3556	8.05
1.5	98.35	93.1	0.4064	--
1.6	74.15	165.1	0.6756	--
1.7	40.49	174.2	0.7620	--

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While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiment, it is to be understood that the invention is not to be limited to the disclosed embodiment, but on the contrary, is intended to cover various

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modifications and equivalent arrangements included within the spirit and scope of the appended claims.

WHAT IS CLAIMED IS:

1. A material comprised of a mass of melt-blown non-woven fibers comprised of a terpolymer of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride monomers.
2. The material of claim 1, wherein the vinylidene fluoride monomer is present in the terpolymer in an amount from about 20 to about 65%.
3. The material of claim 1, wherein the vinylidene fluoride monomer is present in the terpolymer in an amount of about 36.5 wt.%.
4. The material of claim 1, wherein the tetrafluoroethylene monomer is present in an amount from about 30 to about 70 wt.%.
5. The material of claim 1, wherein the tetrafluoroethylene monomer is present in an amount of about 44.6 wt.%.
6. The material of claim 3, wherein the tetrafluoroethylene monomer is present in an amount of about 44.6 wt.%.
7. The material of claim 1, wherein the hexafluoropropylene monomer is present in an amount from about 30 to about 70 wt.%.
8. The material of claim 1, wherein the hexafluoropropylene monomer is present in an amount of about 18.9 wt.%.

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9. The material of claim 5, wherein the hexafluoropropylene monomer is present in an amount of about 18.9 wt.%.

10. The material of claim 6, wherein the hexafluoropropylene monomer is present in an amount of about 18.9 wt.%.

11. The material of claim 1, wherein the fibers are comprised of a blend of the THV terpolymer and at least one other polymer selected from fluorothermoplastic terpolymers different from the THV terpolymer and homopolymers, copolymers, or terpolymers of polysulfones, polyethersulfones, polyarylsulfones, fluorinated polymers, and polyolefins.

12. The material of claim 1, which includes other fibers formed of at least one other polymer selected from fluorothermoplastic terpolymers different from the THV terpolymer and homopolymers, copolymers, or terpolymers of polysulfones, polyethersulfones, polyarylsulfones, fluorinated polymers, and polyolefins.

13. A garment which includes a fabric comprised of the material of any one of claims 1-12.

14. A bandage which includes a fabric comprised of the material of any one of claims 1-12.

15. A bulk air flow vent which includes a fabric comprised of the material of any one of claims 1-12.

16. A filtration medium which includes a fabric comprised of the material of any one of claims 1-12.